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(54) Title: PREPARATION OF ACETIC ANHYDRIDE

(57) Abstract:

A continuous, liquid phase process for carbonylating methyl acetate with carbon monoxide gas in the presence of 2-7 volume percent hydrogen, and a catalytic combination of rhodium and iodine compound and lithium. The use of 2-7 volume percent hydrogen with such catalytic combination in this process reduces tar formation and increases spacetime yields (grams/liter/hours(s)).

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PREPARATION OF ACETIC ANHYDRIDE

This invention relates to a process for the preparation of acetic anhydride. More specifically, this invention relates to a liquid phase process for preparing acetic anhydride by carbonylating methyl acetate in the presence of hydrogen and a catalytic combination of rhodium, an iodine compound and lithium.

It is known that acetic anhydride, a very useful industrial chemical, can be prepared by the carbonylation of methyl acetate. It is also known that the formation of an undesirable by-product, often called "tar" or "soot" is virtually unavoidable in such a carbonylation reaction.

Typically, this tar is formed in the preparation of acetic anhydride by the liquid phase carbonylation of methyl acetate in the presence of rhodium and an iodine compound at elevated temperature and pressure wherein a feed mixture containing methyl acetate is continuously fed to a reaction zone and a mixture containing acetic anhydride is continuously removed. In such a reaction system, tar formation can increase to the point where catalytic activity is greatly diminished and eventually results in termination of the carbonylation reaction.

Available analytical data do not permit absolute identification of the aforementioned tar. Based on combined information of IR (Infrared), H NMR (Hydrogen Nuclear Magnetic Resonance), C NMR (Carbon Nuclear Magnetic Resonance) and elemental analysis, certain aspects of the structure may be proposed; but the poor resolution in the H and C NMR spectra thwart hopes for absolute identification and are suggestive of a highly amorphous material. The C NMR shows two major broad band absorptions of approximately equal intensity, one in the alkyl region ($13\text{--}45 \delta$) and the other in the aromatic region ($120\text{--}140 \delta$). For the same material, the H NMR shows almost no aromatic protons relative to the alkyl bands at .9-1.7 and



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1.6-3.0 δ. In combination, these two spectra suggest a polyalkylated aromatic material substituted to the exclusion of aromatic protons. Additionally, the C'NMR shows some very minor absorptions assignable to carbonyl moieties, a feature 5 strongly suggested by the IR band at 1700 cm⁻¹. The IR also suggests carbon-oxygen (1180 cm⁻¹) and oxygen-hydrogen (36-3300 cm⁻¹) bonds. The elemental analysis substantiates the expectations of aromatic unsaturation showing .60 unsaturations per carbon and an empirical formula of
10 C₃₆H₄₁O₄I₁₅.

Unfortunately, tar formed in the carbonylation of methyl acetate, as previously described herein, increases as reaction conditions, such as temperature and pressure are increased to obtain acceptable space-time yields of acetic 15 anhydride. Space-time yield is the yield of desired product in a unit of time per unit volume of reaction space. It is conveniently expressed in terms of gram/liter/hour(s). It is evident that a carbonylation process of the type described herein, which would combine high space-time yield of acetic 20 anhydride, e.g. a space-time yield of 400 g./l./hr., with suppression of tar formation would represent a significant advance in the art.

The use of catalytic combinations or systems comprising rhodium and an iodine compound in the preparation of 25 acetic anhydride by the carbonylation of methyl acetate has been reported in the patent literature. See, for example, Belgian Patent No. 819,455, granted March 3, 1975 and Japanese Patent Publication Application 75-47922, published April 28, 1970. These publications disclose that the reaction rate can 30 be increased if the catalytic combination contains a promoter such as lithium. In such a process, the lithium is generally added as lithium iodide or lithium acetate.

For purposes of this invention, it is significant to note that neither Belgian Patent No. 819,455 nor Japanese



Published Patent Application 75-47922 disclose including hydrogen gas in the carbonylation reaction.

U.S. Patent 4,046,807, issued September 6, 1977 discloses that tar formation can be suppressed by the inclusion of hydrogen in the gas fed to a carbonylation reactor for preparing acetic anhydride from methyl acetate using a rhodium-containing catalyst with a triphenyl phosphine promoter. There is no disclosure in the patent of using a lithium promoter. Also, Example 13 of the patent clearly indicates that the use of hydrogen gas, as described therein, has a significant detrimental effect upon the yield of acetic anhydride.

Published European Patent Application 0008396, published March 5, 1980 discloses that specific combinations of aliphatic carboxylic acids with heterocyclic quaternary ammonium compounds can be used to increase the catalytic activity of Group VII noble metal-iodine compound compositions in the carbonylation of ethyl acetate. This publication also discloses that up to 10 volume percent of hydrogen gas can be included in the feed gas stream. There is no disclosure of using a lithium promoter in the catalyst system described or of using hydrogen gas in a critical concentration in a carbonylation process to both suppress tar formation and increase the yield of acetic anhydride.

This invention provides a liquid phase process for preparing acetic anhydride by carbonylating methyl acetate by continuously introducing carbon monoxide gas, hydrogen gas and liquid methyl acetate into a reaction zone containing a rhodium containing catalytic combination to thereby form acetic anhydride, and continuously withdrawing acetic anhydride from the zone, characterized in that the amount of hydrogen continuously introduced into the zone is 2-7 volume percent, based on carbon monoxide and hydrogen gases, and said catalytic combination comprises rhodium, an iodine compound and lithium.



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It has been discovered that the use of 2-7 volume percent hydrogen, together with the catalytic combination of rhodium an iodine compound and lithium, as described herein, suppresses tar formation and also significantly increases the reaction rate both in terms of methyl acetate conversion and acetic anhydride production.

The role of hydrogen in this process is not completely understood but it has been examined by infrared spectroscopic monitoring of an ongoing reaction. A batch autoclave coupled with a high-temperature, high-pressure infrared cell, was used to observe the rhodium complexes present during the reaction. In the absence of hydrogen feed the major rhodium species in solution at 175°C. and 800 psig (5616 kPa) is $\text{trans-Rh}(\text{CO})_2\text{I}_4^\ominus$ as evidenced by the metal carbonyl absorption at 2090 cm^{-1} . The pressures indicated in kPa herein are absolute pressures rather than gauge pressures.) A smaller amount of $\text{cis-Rh}(\text{CO})_2\text{I}_2^\ominus$ is also present under these conditions as indicated by the absorptions at 2056 and 1983 cm^{-1} for the carbonyls bonded to rhodium. The addition of hydrogen to the reaction at 175°C. and 800 psig (5616 kPa) results in the rapid disappearance of the infrared absorption at 2090 cm^{-1} for $\text{trans-Rh}(\text{CO})_2\text{I}_4^\ominus$. At the same time, the absorptions for $\text{cis-Rh}(\text{CO})_2\text{I}_2^\ominus$ at 2056 and 1983 cm^{-1} dramatically increase in intensity. The observed transformation of $\text{trans-Rh}(\text{CO})_2\text{I}_4^\ominus$ to $\text{cis-Rh}(\text{CO})_2\text{I}_2^\ominus$ is also accompanied by a substantial increase in the rate of formation of acetic anhydride. On the basis of the infrared spectroscopic measurements it appears that the addition of hydrogen in the process of this invention increases the concentration of active catalyst, $\text{cis-Rh}(\text{CO})_2\text{I}_2^\ominus$.

In practicing this invention, the minimum amount of hydrogen that gives a significant effect is 2 volume percent

based on the total carbon monoxide and hydrogen introduced to the reaction zone. The use of greater than 7 volume percent hydrogen does not significantly improve either the suppression of tar formation or the rate of acetic anhydride formation.

5 The preferred amount of hydrogen used in practicing this invention is 3 to 6 percent, based on total amount of hydrogen and carbon monoxide fed to the carbonylation reaction zone.

In a typical practice of the process, the feed to the carbonylation reactor is such as to maintain within the 10 reaction mixture (1) 250 to 1300 ppm, preferably 500 to 1000 ppm, Rh, (2) 175 to 5000 ppm, preferably 1500 to 3700 ppm, lithium and (3) 7 to 35 weight percent methyl iodide. The remainder of the reactor contents is mostly methyl acetate reactant and acetic anhydride product with minor amounts of 15 by-products such as ethylidene diacetate and acetone. The reactor feed optionally may contain a solvent such as acetic acid, e.g. in an amount that will maintain 5 to 40 weight percent in the reaction mixture. When reaction product is withdrawn in liquid form, the catalyst components, i.e. the 20 rhodium, lithium and iodine as methyl iodide, are recovered from the reactor effluent and are recycled. When necessary, fresh rhodium, as rhodium chloride, rhodium acetate or other rhodium containing compound, and lithium, as lithium hydroxide, lithium iodide, lithium acetate or other lithium-containing 25 compound are added to the catalyst recycle. The fresh rhodium and lithium can be conveniently added as a solution in acetic acid. When the iodine needs to be supplemented it may be added to the system as iodine (I_2), as methyl iodide or, at least in part, as lithium iodide. When reaction product is withdrawn 30 in liquid form, all or essentially all of the rhodium and lithium catalyst components remain in the reactor and, the risk of their depletion from the process is reduced considerably.

The methyl acetate fed to the reactor consists primarily of fresh methyl acetate, which should be essentially

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anhydrous, and some recycled material. The feed may also contain recycled acetic anhydride although it is advantageous to add methanol to any recycled anhydride to convert the latter to methyl acetate feedstock.

5 The process may be carried out at elevated temperatures and pressures in the range of 160 to 220°C. and 300 to 1200 psig. (2170 to 8375 kPa). The particular temperature and pressure employed depends on a number of factors such as the amounts of the three catalysts components
10 that are used, by-product formation, the design of the process system and the space-time yield desired.

The invention is further illustrated by the following examples.

Example 1

15 The reactor consisted of a lower section of five feet, five inches (1.65 m.) of two-inch (5 cm.) diameter pipe, a middle section of six feet, one inch (1.9 m) of one-inch (2.54 cm.) diameter pipe and six feet (1.82 m.) of one-half inch (1.27 cm) diameter pipe. Total reactor volume was 4.95
20 liters. A gas mixture of carbon monoxide and 5 volume percent hydrogen was fed to the reactor through a gas sparger at the bottom of the reactor. Through a reactor feed line, located above the sparger, was fed a mixture containing methyl acetate, acetic acid, acetic anhydride, methyl iodide, lithium and
25 rhodium at an average rate of about 12,600 grams/hour. The reactor contents overflowed from the top of the reactor to a separator where some of the unreacted carbon monoxide and other gases were separated from the liquid and purged from the system. The liquid from the separator passed through a valve
30 which reduced the pressure from about 750 psig (5273 kPa) to 10-20 psig (170-340 kPa). The liquid passed through a flash evaporator, wherein 80-90% of the material was vaporized and entered an evaporator separator (about 1 psig) (108 kPa)

wherein the vapor and liquid were separated. The liquid was mainly acetic acid and acetic anhydride in which the rhodium and lithium catalyst components were dissolved along with minor amounts of methyl iodide and methyl acetate. It was recycled to the reactor. The vapors from the evaporator separator were fed to a column in which the temperature was maintained at about 140°C. at the base and about 100°C. at the top. Crude acetic anhydride suitable for further refining was removed from the lower portion of the column. The lower boiling components (methyl acetate, methyl iodide and some acetic acid) were taken overhead and fed to a tank to which makeup methyl acetate was also fed. The contents of the tank were continuously fed to the reactor feed line.

Using the above-described system, acetic anhydride was produced by the carbonylation of methyl acetate at about 190°C. and 750 psig (5273 kPa). Over the course of 80 hours of continuous operation samples of the liquid from the separator and the reactor feed periodically were analyzed and the conversion of methyl acetate (methyl acetate fed minus methyl acetate in the separator liquid divided by methyl acetate fed) and the acetic anhydride space-time yield (STY, in grams/liter/hours) were determined. The data thus accumulated is shown in Table I. The hydrogen in the gas feed was stopped at hour 245 and was resumed at hour 267. As indicated by the conversion and space-time yield data in Table I, there was no significant tar formation during the period of time when hydrogen gas was fed to the reactor.

The data of Table I show that discontinuing the hydrogen feed to the carbonylation reactor has a substantial detrimental effect on production rate, i.e. space-time yield.



Table I
Reactor Separator Pot Underflow Composition

Operating Time, Hours	Rh ppm	Li ppm	Methyl Iodide %	Methyl Acetate %	Acetic Acid %	Anhydride Acetate %	Acetic Anhydride %	Methyl Acetate %	Conver- sion %	Space-Time Yield (8 hour Average)
223	-	-	-	-	-	-	-	45.9	20.8	-
227	504	3121	16.0	16.9	16.7	46.8	42.5	21.3	60	650
231	-	15.5	17.0	20.0	43.4	41.0	19.4	59	-	-
235	790	3587	15.4	8.6	33.2	39.4	27.3	21.9	68	606
243	593	3206	19.1	9.9	23.3	41.9	25.3	24.1	61	482
247	-	27.2	17.0	27.3	28.9	20.7	13.5	14	-	-
251	482	2802	21.0	21.4	26.8	26.3	37.4	11.9	63	254
255	-	19.7	22.4	30.3	25.7	45.9	9.5	51	-	-
259	308	1634	25.0	15.4	32.9	21.8	38.4	6.9	60	292
267	474	2451	22.2	22.0	33.0	20.3	30.1	9.0	24	223
271	-	21.0	16.5	23.3	34.9	31.0	15.9	47	-	-
275	450	2260	20.4	14.0	20.0	34.9	29.7	18.7	50	401
279	-	21.0	18.6	23.1	34.1	35.0	15.5	47	-	-
283	469	2375	21.9	17.5	22.9	34.0	45.7	13.2	62	435
291	905	3955	23.4	24.1	19.9	31.3	49.7	8.0	52	309
295	-	18.6	24.9	18.9	36.3	37.5	16.2	34	-	-
299	408	2216	16.7	17.0	25.9	35.3	30.9	17.4	42	358



Example 2

Four runs in which varying amounts of hydrogen were fed to the carbonylation reactor were carried out in the apparatus described in Example 1 except that the reactor consisted of the five feet, six inches, (1.7 m.) of pipe having a volume of 3.5 liters. The temperature was about 190°C., the pressure about 750 psig (5273 kPa) and the feed rate about 12,600 grams/hour over the course of each run. In Table II are set forth average values for each run, the composition of the feed stream (weight percent), the rhodium and lithium (ppm) present in the system, the amount of hydrogen (H_2) fed (volume percent of the total gas fed), the acetic anhydride space-time yield (STY; grams/liter/hour) and the weight ratio of ethylenediacetate (EDA) to acetic anhydride (Ac_2O) produced. The duration of the first run was 64 hours, the second 65.5 hours, the third 73 hours and the fourth 34 hours.

In Runs 1-3, high space-time yields were obtained although the higher concentrations of hydrogen resulted in the formation of significant amounts of ethylenediacetate. Also, in these runs, the tar formation was minimal and could be easily handled. In Run 4, essentially no ethylenediacetate was formed but the space-time yield of acetic anhydride was decreased considerably by the use of only 1.2 volume percent hydrogen in the gas feed (less than the amount of hydrogen required by this invention).

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Table II
Reactor Feed Composition

<u>Run</u>	<u>Methyl Chloride</u>	<u>Methyl Acetate</u>	<u>Acid Ac₂O</u>	<u>EDA</u>	<u>LiB</u>	<u>H₂</u>	<u>STY</u>	<u>EDAI/Ac₂O</u>		
1	15.0	50.4	20.4	12.0	0.38	607	2098	6.25	573	0.0111
2	14.0	51.9	16.8	15.9	0.39	696	1977	4.33	564	0.0079
3	16.0	39.8	27.1	17.7	0.18	812	2430	2.23	541	0.0033
4	13.1	30.3	35.2	13.2	0.04	817	2281	1.20	342	0



Example 3

Seven runs were carried out in a 1.83 liter autoclave fitted with Hastelloy B-2 baffles. Mixing was provided by a magnetic stirring bar operated at about 630 rpm. To permit obtaining liquid samples of the reaction mixture under the reaction conditions, the autoclave was equipped with a Hastelloy B-2 dip tube having the necessary valve system to permit safe removal of liquid under pressure. The temperature of the reaction mixture was monitored by an iron constantan thermocouple placed in a thermowell immersed in the liquid.

Constant pressure was maintained throughout each run. The solid catalyst components and the liquid reactants were placed in the autoclave. After sealing and pressure testing, the mixture was flushed with carbon monoxide by pressurizing to 100 psig (790 kPa) with stirring followed by slowly venting to atmospheric pressure. After a second pressurization-vent cycle, the autoclave was pressurized to 10 psig (170 kPa) with the reactant gas and then heated to the desired temperature.

An aliquot of the reaction mixture taken at this point was used as a zero time sample. Immediately following the initial sampling, the autoclave was pressurized to the desired value with the reactant gas. The course of the reaction was followed by removing aliquots of the reaction mixture at 30 minute intervals while maintaining reaction conditions. To ensure representative sampling, the second of two 5-ml aliquots taken at the specified sampling time was used to obtain analytical data.

The aliquot samples were cooled and analyzed directly by gas chromatography using butyronitrile as an internal standard. Data for each sample was obtained in terms of milligrams of component per gram of solution. Based on the assumption that the weight increase of the reaction mixture during the run was due only to the weight of carbon monoxide



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used to produce acetic anhydride (Ac_2O) the following formula was used to calculate the total moles of acetic anhydride present at the sampling time..

$$5 \quad \text{moles}_{\text{Ac}_2\text{O}} = \left[\frac{\text{W}_0}{1 - \frac{28}{102} \times \text{x}_{\text{Ac}_2\text{O}}} \right] \frac{\text{x}_{\text{Ac}_2\text{O}}}{102}$$

W_0 = initial weight of reaction mixture

$$10 \quad \text{x}_{\text{Ac}_2\text{O}} = \frac{\text{mg Ac}_2\text{O}}{\text{gm Solution}} \times 10^{-3}$$

Runs 1 and 2 were carried out at 175°C. and 650 psig (3918 kPa) using (1) a gas feed of carbon monoxide without hydrogen and carbon monoxide containing 5 volume percent hydrogen and (2) the following materials:

15	$\text{RhCl}_3 \cdot \text{xH}_2\text{O}$	1.24 g.
	LiI	33.85 g.
	Acetic Acid	220.50 g.
	Methyl Acetate	676.50 g.
	CH_3I	130.20 g.

20 Runs 3 and 4 were conducted at 190°C. and 1000 psig., (6996 kPa) with and without hydrogen in the carbon monoxide feed using the following materials:

	$\text{RhCl}_3 \cdot \text{xH}_2\text{O}$	0.62 g.
	LiI	25.39 g.
25	Acetic Acid	220.50 g.
	Methyl Acetate	676.50 g.
	CH_3I	130.20 g.

In each of Runs 5, 6 and 7, 8, 9 and 10 volume percent

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hydrogen respectively, were present in the carbon monoxide fed to the autoclave. These runs were carried out at 200°C. and 1000 psig (6996 kPa) using the following materials:

	RhCl ₂ .xH ₂ O	0.30 g.
5	LiI	12.30 g.
	Acetic Acid	220.50 g.
	Methyl Acetate	676.50 g.
	CH ₃ I	130.20 g.

The results, shown in
10 Table III, obtained from Runs 1-7 show that the inclusion of hydrogen in the carbon monoxide used to carbonylate methyl acetate substantially increased the rate at which acetic anhydride was formed. Runs 6 and 7 further show that the use of 10 volume percent hydrogen in the carbon monoxide did not
15 increase the rate over that observed when 5 volume percent hydrogen was used. No significant quantities of tar were formed in runs 1-7, made according to the practice of this invention.

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Table III

Time, minutes	Run 1	Run 2	Run 3	Run 4	Run 5	Run 6	Run 7
	No H ₂	5% H ₂	No H ₂	5% H ₂	No H ₂	5% H ₂	10% H ₂
30	0.41	0.75	0.57	1.03	0.44	-	0.86
60	1.07	2.06	1.61	2.30	1.28	1.56	1.70
90	1.75	3.05	2.60	3.42	1.95	2.30	2.47
120	2.40	4.10	3.48	4.36	2.49	3.10	3.20
150	3.25	4.85	4.35	5.36	3.04	3.90	3.96
180	3.91	5.47	4.98	6.07	3.57	4.43	4.50
210	4.44	6.27	5.63	6.80	3.87	4.94	5.06
240	5.03	6.74	6.00	7.25	4.31	5.03	5.72
270	5.60	7.25	6.55	7.43	4.68	6.15	6.20
300	6.10	7.56	6.82	7.08	-	-	-



Example 4

A 300 cc autoclave was fitted with a dip tube and the necessary valve system to permit safe removal of liquid under pressure as in Example 3. The following were charged to the 5 autoclave: $\text{RhCl}_3 \cdot x\text{H}_2\text{O}$, 0.95 g; LiI, 13.0 g; CH_3I , 6.10 g; acetic acid, 40.0 g; methyl acetate 144.0 g. The autoclave was sealed, pressure tested, and flushed with carbon monoxide as in Example 3. The autoclave was pressurized to 10 psig (170 kPa) with carbon monoxide and heated to 175°C. After 10 pressurizing to 800 psig (5617 kPa) with carbon monoxide, samples are taken at 20 minute intervals. Immediately following the sampling at 120 minutes, the autoclave pressure was raised from 800 psig (5617 kPa) to 1,000 psig (6996 kPa) by the addition of hydrogen.

15 The total pressure was then allowed to drop to 800 psig (5617 kPa) before additional carbon monoxide was added to maintain 800 psig (5617 kPa) total pressure. The results, set forth in Table IV, show that the addition of H_2 substantially increased the rate of production of acetic anhydride (Ac_2O). In addition, no significant quantity of tar was formed over the 20 course of the reaction.

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Table IV

<u>Time, (Minutes)</u>	<u>Ac₂O (Moles)</u>
20	0.06
40	0.08
5	60
	0.13
	80
	0.19
	100
	0.26
	120*
	0.31
	140
	0.53
10	160
	0.76
	180
	0.97
	200
	1.12
	220
	1.25

*H₂ added immediately after sample was taken.

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Claims:

1. A liquid phase process for carbonylating methyl acetate to form acetic anhydride which process comprises,
 - a) continuously introducing into a reaction zone, carbon monoxide gas, hydrogen gas in an amount of 2-7 volume percent, based on carbon monoxide and hydrogen gases, and liquid methyl acetate,
 - b) carbonylating methyl acetate within the zone in the presence of rhodium, and iodine compound and lithium to thereby form acetic anhydride within the zone, and
 - c) continuously withdrawing acetic anhydride from the reaction zone.



III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category	Citation of Document, ¹⁶ with indication, where appropriate, of the relevant passages ¹⁷	Relevant to Claim No ¹⁸
(CONTINUED)		
A	BE, A, 819455, Published 03 March 1975	1
A	ZA A, 761482, Published 12 September 1977	1
A	JP, A, 77-3926, Published 31 January 1977	1

INTERNATIONAL SEARCH REPORT

International Application No PCT/US81/01289

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) ^{1,4}

According to International Patent Classification (IPC) or to both National Classification and IPC
 Int. Cl. ³ C07C 51/56
 U.S. Cl. 260/549

II. FIELDS SEARCHED

Minimum Documentation Searched ⁴

Classification System	Classification Symbols
U.S.	260/549

Documentation Searched other than Minimum Documentation
 to the Extent that such Documents are Included in the Fields Searched ⁵

III. DOCUMENTS CONSIDERED TO BE RELEVANT ^{1,4}

Category ⁶	Citation of Document, ^{1,6} with indication, where appropriate, of the relevant passages ^{1,7}	Relevant to Claim No. ^{1,8}
X	US, A, 4,046,807, Published 06 September 1977, see column 1, lines 64-66, Kruckertz	1
X,P	US, A, 4,252,741, Published 24 February 1981, see column 3, lines 14-20; column 4, lines 22-36; column 6, lines 25-31; and column 7, lines 5-34, Porcelli et al	1
X	GB, A, 2,013,184, Published 08 August 1979, see page 3, lines 36-44	1
X	N, Derwent Abstracts, Showa Denko KK, "Acetic anhydride from methyl acetate and carbon- monoxide-by contacting in presence of rhodium catalyst", Japan 75-47921	1
X	N, Derwent Abstracts, Showa Denko KK, "Acetic anhydride manufactured from methyl acetate and carbon monoxide-in presence of rhodium catalyst", Japan 75-47922	1
A	US, A, 3,579,566, Published 18 May 1971, Fenton	1
A	N, Chem Tech, issued October 1971, "Low pres- sure process for acetic acid via carbonyla- tion", see page 600, Roth et al	1

* Special categories of cited documents: ^{1,9} "P" document published prior to the international filing date but on or after the priority date claimed

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IV. CERTIFICATION

Date of the Actual Completion of the International Search ²:

03 November 1981

Date of Mailing of this International Search Report ²:

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